ABSTRACTS

TECHNOLOGY TRANSFER CONFERENCE No.4

NOVEMBER 29&30 ,1983

SPONSORED BY

THE RESEARCH ADVISORY COMMITTEE

MINISTRY OF THE ENVIRONMENT

ONTARIO

AT THE CONSTELLATION HOTEL ,TORONTO

This year, the Air Resources Branch Seminar is consolidated with the annual Technology Transfer Conference to present the audiences of the two conventions with a broader range of research activities on air, water, waste, methodology, and the health effects of environmental pollution.

POLICY & PLANNING BRANCH

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Acknowledgements

The Ministry of the Environment's Research Advisory Committee would like to acknowledge the cooperation and efforts of the authors and Ministry staff who contribu to the organization of the Conference.

The financial support of the Provincial Lottery Trust Fund for environmental health-related research in Ontario has largely contributed to the success of this program including its technology transfer.

Number 1

The Feasibility of the Sterile Male Approach to Control the Onion Maggot

F.L. McEwen, G. Ritcey and J. Madder

Abstract

The potential of the sterile insect release method for control of the onion maggot was evaluated from 1981 to 1983. The techniques necessary for mass rearing, sterilization, marking, release and evaluation were developed during the early part of the program. These techniques were tested in a trial release of one million flies on 40 hectares of onions in 1982. The techniques were refined and used in 1983 for release of nine million flies on 100 hectares in the Keswick Marsh. In 1983, two releases of 4.5 million flies were made during the second and third weeks of July to coincide with the flight of the second generation of the onion maggot. Following the release, fertility of the wild population declined by 30-45% for two weeks. Damage due to the second generation was similar in the fields where these flies were released and in fields which received a normal insecticide program. On a biological basis, the sterile male release technique is a feasible method for control of the onion maggot, however, its high cost would make it an unlikely candidate for a practical control program.

DEVELOPMENT OF METHODS FOR THE DETECTION OF ROTAVIRUSES

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Rotavirus is the major etiological agent of infantile gastroenteritis, and is associated with up to 50% of the hospitalized cases of diarrheal illness in infants and young children. Between 1972-1979 there were 26 fatal rotavirus infections recorded at Toronto's Hospital for Sick Children. Because large quantities of virus are shed in the stool during infection, and because of the hardy nature of the virus, it is not surprising that rotavirus pollution of public water has become a matter of considerable concern. Sensitive virus detection methods are essential for monitoring the distribution of rotavirus in the environment. It has been the objective of this project to develop laboratory methods for the detection of rotavirus, and to design these methods so that they could be applicable to environmental samples.

In the initial phase of the project, simian rotavirus SA-11 was used as the virus model, and methods were investigated for detecting small quantities of rotavirus that had been isolated in cell cultures. Two new light microscope methods were developed: (1) the SPA method employing fixed Staphylococcus aureus cells as morphological markers; (2) a fluorescent antibody method (LAB) utilizing the high affinity of avidin for biotin. Both methods were compared with the more commonly used indirect immunofluorescence method (IIF).

The LAB method was found to offer the greatest sensitivity. It could detect, after 24 hours incubation, intracellular multiplication of an inoculum as low as 100 $TCID_{50}$, whereas the minimum inoculum size detectable by SPA was 125, and by IIF was 170. When approximately 20,000 $TCID_{50}$ of rotavirus was inoculated into cell cultures, its presence could be detected at 4 hours by LAB, 1 hour earlier than by the other two methods.

Current procedures for detecting viruses in the environment rely heavily on cell culture isolation. But by this approach there is danger of excluding several important viruses which do not grow readily in cell culture. Best known of these fastidious viruses are hepatitis A virus, Norwalk virus, certain strains of adenovirus, and human rotavirus. The next phase of this project should concern itself with the application of methods such as the LAB method, as well as immunoelectron microscopy and enzyme-linked immunosorbent assay (ELISA), for direct detection of viruses in environmental samples, thus bypassing the extremely useful but highly selective cell culture isolation step.

THE EPIDEMIOLOGY OF SWIMMING - RELATED ILLNESS AT SELECTED CONSERVATION AREAS

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During the summers of 1979, 1980, and 1982 swimmers and non-swimmers were interviewed in prospective cohort epidemiological - microbiological studies carried out at beaches in Ontario. Of more than 8,000 people interviewed, 9.4% of the swimmers became ill versus 3.4 to 3.7% of the non-swimmers. Swimmers experienced respiratory ailments most frequently followed by: gastrointestinal, eye, ear, skin, and allergic symptoms, respectively. Water samples collected at the beaches were routinely analyzed for fecal coliforms, fecal streptococci, total staphylococci, and viruses and, in most surveys, for heterotrophic bacteria and Pseudomonas aeruginosa organisms as well. In 1980, viruses were isolated from the water at two conservation area beaches but not from the water of any of the Great Lakes beaches surveyed. Morbidity among swimmers was shown to be related to staphylococcal counts ($p < 0.0004$) and fecal coliform levels ($p < 0.0058$). Data from a 1983 study which was conducted at Boyd, Claireville, Heart Lake, Kelso and Albion Conservation Areas and at Professor's Lake in Brampton will be used to augment the results from previous surveys.

Number 4

ABSTRACT

A New Potable Water Treatment Method for Trihalomethane Precursor and Synthetic Organic Removal

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Zenon Environmental Inc.

Coagulation is widely used in potable water treatment for the removal of turbidity causing particles. This study investigated the potential of the coagulation process for organic removal, both natural and synthetic. A wide variety of conventional coagulants, recently developed pre-polymerized coagulants and flocculants were studied, with the aid of jar tests.

Results indicate that coagulants are generally highly effective in removing natural organics. Synthetic organics on the other hand do not appear to be removed by coagulation.

As much as 80% of the natural organics present in the water can be removed by coagulation. Consequently, trihalomethane formation, due to chlorination, can be substantially reduced. The operating pH was found to have a significant effect on the removal of organics and also the formation of trihalomethanes. Maximum organic removal typically occurred in the pH range of 5.0 to 6.0. The lowest trihalomethane formation per unit weight of TOC typically occurred at pH 6.0 or below. However, for the aluminum based coagulants, the optimum pH was found to be between 6.0 and 7.0. Above and below these pH's residual aluminum in the water often exceeded the MOE guideline of 0.1 mg/L.

Results of jar tests and filtrability tests showed that the pre-polymerized coagulants both settled and filtered more readily.

A Full-Scale Study of Ultraviolet Disinfection of Secondary Effluent

Garry Palmateer[1], Walter G. Cook[1], G. Elliott Whitby[2], Jan Maarschalkenweerd[2], Doug Huber[1], Ken Flood[3]

A full-scale gravity flow UV system which consists of a series of modules which form two separate rectangular matrices of UV lamps was placed in each effluent channel of a conventional secondary sewage treatment plant.

Photoreactivation and dark repair experiments showed that 3h produced the maximum number of total and fecal coliforms whereas fecal Streptococci showed no increase.

Routine bacteriological sampling has shown that the geometric mean of the total and fecal coliform bacteria before and after photoreactivation can be maintained below the limits of 2,500 and 200 organisms per 100 ml respectively after the UV units and in between the two matrices. The chlorinated effluent was similar bacteriologically except for the resistant spore-forming bacteria, Clostridium perfringens, and bacteriophage of Escherichia coli C which were more sensitive to UV irradiation.

A fish toxicity evaluation conducted in the receiving steram showed that chlorinated effluent was toxic to rainbow trout where UV irradiated effluent was not.

A cost comparison has shown that UV disinfection is a cost effective alternative to other forms of wastewater disinfection such as chlorination, chlorinaton-dechlorination and ozonation.

The UV and chlorinated effluents have been tested for the following pathogens: Pseudomonas aeruginosa, Yersinia enterocolitica, Campylobacter jejuni and Salmonella sp.

At the present time the UV system is being subjected to increased solids simulating by-pass and poor-settling conditions.

Although research continues, at least 14 UV systems are in operation or being installed or planned for at sewage treatment plants in the United States.

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Number 6

MEASUREMENT OF INFILTRATION THROUGH LANDFILL COVERS

BY

P.K. LEE, GARTNER LEE ASSOCIATES LIMITED
A.G. HIMS, GARTNER LEE ASSOCIATES LIMITED
DR. GILHAM, UNIVERSITY OF WATERLOO

The usual source of landfill leachate is related to the infiltration of precipitation through the soil cover and then refuse. The prediction of infiltration through landfill surface covers is often qualitative and is poorly documented. Minimal data are available to assess the effectiveness, reliability and design of current and past practices relative to leachate production. A two phased study, of which this is the first, is to be carried out over a three year period. The objectives of Phase I reported here are to design a suitable lysimeter applicable to a variety of landfill environments that will provide economical, repeatable and accurate measurements. In Phase 2 a number of variables and settings will be documented. A literature search and review was the initial task undertaken and provided the basis for design. Installations were constructed at the Brittania Road Landfill in Mississauga in the Region of Peel. This site is an engineered facility with cells constructed and based in low permeability clay subsoils. The landfill is a containment site with provisions for leachate collection and treatment. The final soil cover is a compacted silty clay. Two types of lysimeters are reported upon, one being of a sophisticated data accumulation type including a storage well and an automatic data recording mode while the other is a simple sheet lysimeter. The storage well lysimeter has met the objectives.

The paper presents details of both designs along with installation and operation aspects and problems. Data accumulated since March, 1983 are presented along with preliminary analysis and recommendations.

Sept. 16, 1983.

Number 7

Abstract

The Use of Marshlands In Wastewater Treatment

S. A. Black
Ministry of the Environment

The use of aquaculture concepts for wastewater treatment is receiving increased attention. Systems studied to date, have included both natural and artificial marshlands, ponds, raceways and other structures based upon various combinations of rooted and free-floating vegetation. The use of both artificial and natural marshlands for the treatment of municipal wastewater is being actively evaluated in Ontario.

This paper defines the current status of marshland treatment technologies and evaluates their potential for routine use in municipal wastewater treatment. In so doing, the paper presents an update of the ongoing research studies at the Listowel artificial marsh facility and outlines details of the Bradford natural marsh study, the Cobalt Artificial Marsh Study and the Port Perry marshland treatment demonstration project.

Number 8

Abstract for

Ontario Ministry of the Environment Technology Transfer Meeting

Tuesday, November 29, 1983

3:15 p.m.

THE HAMILTON STUDY: RELATIONSHIP BETWEEN OUTDOOR AND INDOOR AIR QUALITY IN HOMES AND ELEMENTARY SCHOOLS

L.D. Pengelly, W. Furlong, C. Goldsmith, and S. Toplack

Measurements have been made of indoor and outdoor levels of nitrogen dioxide (NO_2), sulphur dioxide (SO_2) and suspended particulate material (SPM) using a multipollutant sampler which we have developed (1). Observations were made for two 5-day sessions at each site, once during the heating season (H) and once during the non-heating season (NH). Paired indoor and outdoor observations were made during the same 24-hour sampling period at each site using the same instrumentation. Complete sets of paired data were obtained for 16 schools in both seasons, for 20 homes in the non-heating season and 14 of that 20 in the heating season. Data were much more difficult to obtain from homes than schools. The study showed patterns of results which were systematic for each pollutant, but differed between pollutants. Most of the results reported here will be in terms of indoor-outdoor ratio (I/O) expressed as percent, in the non-heating or heating season. For NO_2, in schools the I/O ratio was close to 75%, and was found to be independent of heating season, with indoor levels strongly correlated with outdoor levels. In homes, the I/O ratio depends on the presence of indoor sources, such as smokers, or gas stoves. In the absence of these, there is relatively little effect of heating season, and the ratio is about 80%. Smokers were not found to have an effect on indoor NO_2 levels in either season, but gas stoves were associated with markedly increased ($P < 0.001$) levels of NO_2 in both seasons, contributing an additional 13 ppb (NH) and 25 ppb (H). This resulted in homes with gas stoves having an I/O ratio of 1.8 (NH), 2.1 (H).

For SO_2, in schools, the I/O ratio was about 22%, independent of heating season, indoor levels being correlated with outdoor levels ($P<0.01$). In homes, the indoor level depends on heating season, and is poorly correlated ($P>0.05$) with outdoor levels in either season. The I/O ratio = 64% (NH), 15% (H) (SE 13%). For SPM, in schools, I/O ratio was 90% (NH), 140% (H), but there was no significant correlation with outdoor levels or season. In homes, I/O ratio was 134% (NH), 101% (H). In the non-heating season there was no significant correlation with outdoor levels, or the presence of smokers. In the heating season, there were significant effects from outdoor levels and smokers. The presence of smokers added 35 $\mu g/m^3$ of particulate to indoor levels.

The results of this study show that in schools, both for NO_2 and SO_2, indoor levels are well correlated with outdoor levels, independent of heating season, whereas indoor particulate levels are variable, frequently higher than outdoor levels, and uncorrelated with outdoor levels or heating season.

In homes without indoor sources for NO_2, there is little effect of heating season, and the indoor levels are correlated with outdoor levels. Gas stoves are a major indoor source, giving rise to indoor concentrations double the outdoor concentrations, during both heating and non-heating seasons. Levels of SO_2 are low indoors, poorly correlated with outdoor levels, and strongly dependent on heating season, being much lower during the heating season. Suspended particulate material levels indoors were generally higher than outdoors, and poorly correlated with outdoor levels in either season. During the heating season, however, the presence of smokers contributed substantially ($P<0.01$) to the particulate load, but had no effect on the NO_2 or SO_2 levels.

(1) Pengelly, L.D., A.T. Kerigan, C.H. Goldsmith, W. Furlong, W. Spurgeon, S. Toplack. A multipollutant sampler for indoor and outdoor ambient air. Proc. (Int.Symp. on Indoor Air Poll'n, Health and Energy Conservation) Session C2, No.11. Harvard Univ. JFK School of Gov't & School of Public Health. Amherst, Mass;Oct. 13-16, 1981.

Number 9

COMBINED APPLICATION OF OZONE AND CHLORINE OR CHLORAMINE TO REDUCE PRODUCTION OF CHLORINATIED ORGANICS IN DISINFECTION OF HIGH DOC DRINKING WATERS

J. L. Robertson - IEC Beak Consultants Ltd.

ABSTRACT

The application of ozone as the primary disinfectant was investigated on water supplies in Ontario containing high concentrations of dissolved organic carbon (DOC), as a means to reduce elevated levels of trihalomethanes and other chlorinated organics. Laboratory and pilot plant studies demonstrated that the use of ozonation to replace pre-chlorination resulted in substantially reduced THM and NPOX concentrations with subsequent post-chlorination, as compared to conventional pre- and post-chlorination. THM and NPOX production were found to be negligible if ozonation was combined with chloramination as the secondary disinfectant. Batch tests showed that these conclusions applied to another high DOC water supply, although the THM and NPOX production per unit of DOC varied between water supplies. This demonstrated the need for pilot studies on individual water supplies to develop data for process design. Preliminary cost estimates for various sizes of ozonation plants were prepared to assess the general economics of adding ozonation to existing water treatment plants. The study concluded that ozonation combined with controlled post-chlorination or chloramine application, represented an effective strategy for control of THM and NPOX in high DOC waters while maintaining bacteriological quality and providing colour reduction and taste and odour control.

Number 10

Chemical Identification and Biological Assay Studies of Environmental Mutagens, Promoters and Inhibitors

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ABSTRACT

Chemical Identification and Analysis

The studies of chemical identification and analysis of environmental pollutants involved polynuclear aromatic hydrocarbons (PAH) in water samples. The methods under investigation included removal of the organics in the water samples by solvent extraction or by C_{18} Sep-Pak cartridges, followed by elution of the adsorbed PAH (from the Sep-Pak) with tetrahydrofuran (THF). The THF extract was evaporated to a small volume in a Kuderna-Danish evaporator under a stream of nitrogen. After addition of acetonitrile to a sample volume of 2 ml, the analysis was carried out by HPLC, using reversed phase columns, various percentages of acetonitrile in water as the mobile phase under isocratic conditions and spectrophotometric detection. Identification was accomplished by the use of PAH standards, consisting of 16 compounds listed as priority pollutants by the U.S. Environmental Protection

Agency. Data recording was accomplished by a computing integrator. Mass spectra of PAH were also determined for identification purposes.

Water samples from the Welland River, collected at the steel bridges opposite the City of Welland and at Wellandport, were analyzed for eight PAH compounds. These were detected in much higher concentrations at Wellandport than in the samples at the City of Welland. The contaminants included the following carcinogens and mutagens:- benzo(a)pyrene, dibenz(a,c)anthracene, dibenz(a,h)anthracene, benzo(g,h,i) perylene and indeno(1,2,3-cd)pyrene.

A procedure has been developed to improve greatly the efficiency of extraction of PAH from water samples by C_{18} Sep-Pak cartridges involving the acidification of the water samples to pH 2 and prior activation of the Sep-Pak with THF. Recoveries of PAH ranged from over 80 to nearly 100 percent.

Biological Assay Studies

The biological studies of mutagens, potential inhibitors and promoters have been conducted by means of a three-tier system of assays, consisting of the Ames Salmonella typhimurium test, and the *in vivo* bone marrow micronucleus and abnormal spermhead assays on mice. These assays have proved useful in delineating the mutagenic activity of representative PAH, such as 7,12-dimethylbenz(a)anthracene (DMBA), benzo(a)pyrene (BaP) and other chemicals, acting singly and in pairwise combintaions. The mutagenic response of pairwise mixtures of promutagens such as BaP and DMBA or the other strong PAH mutagens was non-additive. However, the combination of a direct-acting mutagen such as mitomycin C (MMC) and BaP, yielded an additive response. Moreover, the combination

of the promutagens BaP and cyclophosphamide (CP) was found to be additive. CP induces a different enzyme system and metabolic pathway than that of BaP. Combinations of a direct-acting mutagen and a promutagen or of two promutagens that act by different enzymatic pathways (e.g., BaP and CP) were found to yield an additive clastogenic response in both somatic and germ cells.

A considerable number of complex phenols and antioxidants have been tested to determine their effectiveness as inhibitors of mutagenesis. Studies of inhibitors reported in the literature have been confined mainly to an assessment of their role in preventing or reducing neoplasia by carcinogenic agents. However, we have found that a number of such substances, e.g., butylated hydroxyanisole and cysteamine, which have been cited as effective inhibitors of chemical carcinogenesis, show no degree of inhibition whatever against the mutagens DMBA, BaP, CP and others, when tested by means of the in vivo bone marrow micronucleus assay. However, effective inhibition against the mutagenic effects of DMBA and BaP has been demonstrated by 7,8-benzoflavone, 5,6-benzoflavone, ascorbic acid, caffeic acid, ethoxyquin, disulfiram, α-tocopherol and β-sitosterol, corn oil and sunflower oil.

Preliminary studies have been conducted to determine the effects on PAH mutagens of promoters such as arochlor, phenobarbital and hexachlorobenzene, using the in vivo bone marrow micronucleus and abnormal spermhead assays.

Number 11

Collaboration Study on Short-term tests for Genotoxicity and Carcinogenicity.

Dave Logan* and M. F. Salamone**

Abstract

An international genotoxicity and carcinogenicity study was established jointly by the World Health Organization, the United Nation Environment Programme and the International Labour Office. Our role in this programme was to provide data on the genotoxic action of 4-6 selected chemicals as determined with the in vivo bone marrow micronucleus assay and the mammalian in vivo abnormal spermhead assay. The chemicals selected for the in vivo assays were benz(a)pyrene, pyrene, 2-acetylamino fluorene, 4-acetylamino flourene, hexamethylphosphoramide and O-toluidene. In addition to these chemicals six other were selected to undergo the same test rigor. These were priority pollutants selected by the various branches of the MOE. The chemicals were trichloroethylene, pentachlorophenol, mirex, chlorobenzene, atrazine and ethylene dichloride. Results on each of the above chemicals are reported.

An additional ten chemicals from the international study were used in the validation of the sister chromatid exchange and replicative killing assays. Results on some of these chemicals are reported.

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** Biohazards Laboratory, Ministry of the Environment.

SUPPRESSION OF IMMUNE DEFENCES BY HALOGENATED AROMATIC HYDROCARBONS

D.A. Clark, J. Gauldie, and G. Sweeney, Host Resistance Program, Departments of Medicine and Pathology, McMaster University, Hamilton.

Chemical assay methods now permit detection of exquisitely low levels of haloaromatic hydrocarbons such as dioxin in the environment raising concerns as to the long term effects of chronic exposure on the general public. Although the best definition of a "safe" level of exposure can be debated, it is our view that such a definition will have to be based on the demonstration of "zero biological effect". Epidemiological surveys of exposed human populations (i.e. Seveso and dioxin exposure) require an excessive period of observation to assess long term effects, deal with a genetically heterogeneous population in which the degree of exposure (the dose) has not been controlled, and require large numbers of individuals be followed to detect toxic effects of low frequency.

Study of haloaromatic hydrocarbon toxicity in animals has focused primarily on dioxin of which 2,3,7,8-tetrachlorodibenzo-p-dioxin or TCDD has been of primary interest. In a variety of species, the immune system has been found to be particularly sensitive to TCDD. For example, exposure of guinea pigs to 1 mcg/kg TCDD produces rapid death associated with atrophy or shrinkage of the thymus gland which is a key organ in the development of the thymus-derived or T cells of the immune defence system. Since the immune system of the laboratory mouse is similar to that of man and their short lifespan allows one to obtain data concerning chronic toxicity, and since inbred strains are available in which the genetic basis determining susceptibility to TCDD has been defined, we elected to examine the effects of TCDD in this species. The results of our investigations done over the past 4 1/2 years may be summarized as follows:

1. Although all types of immunity may be compromised by large doses of TCDD, the murine T cell mediated immune system that produces killer T cells that lyse some types of virus-infected cells and some types of tumors is exquisitely sensitive to suppression. Animals given 4 ng/kg (4 parts per trillion) appear healthy but have impaired immune responses in vitro.

2. This impaired immunity is associated with an increased mortality following challenge with herpes virus type II.

3. TCDD does not act directly on T lymphocytes but rather indirectly through non-lymphoid cells to promote the generation of a second type of T cell, a suppressor T cell, that prevents killer T cell production. Although TCDD may also act on the liver to induce mixed function oxidase enzymes, the immune system is 10-100 times more sensitive to TCDD.

4. The induction of suppressor cells in the mouse by TCDD may be reflected in an increase in the number of lymphocytes bearing the Ly 2 surface marker. A similar marker is present on human lymphocyte suppressor T cells.

5. Other types of haloaromatic hydrocarbons such as Aroclor 1254 and 3,4,3',4'-tetrachlorobiphenyl also suppress killer T cell generation in the mouse through a mechanism that is similar to that of TCDD.

We hypothesize that measuring suppression of the killer T cell response in man or changes in the lymphocyte/suppressor cell sub-populations might provide a sensitive test for the biological effects of haloaromatic hydrocarbon exposure on the immune system.

Pamela Stokes and Lisa Richman, University of Toronto

Abstract

Partitioning of Mercury, Lead and Cadmium in Aquatic Systems, in Relation to Acidification

Acidification has the potential to modify the solubility and/or the chemical speciation of metals, whether or not there is any external loading of metal into an aquatic system. The present study relates to three of the metals which are of concern: mercury, lead and cadmium. It excludes local or point sources of metal and focusses on soft water systems which are impacted by acidic precipitation.

An inverse correlation had already been demonstrated in a number of field studies between pH of water and mercury in certain species of fish. Recent field surveys conducted by our labs showed that filamentous algae in lakes accumulated mercury in the same pattern. There was a significant correlation between mercury in yearling perch and mercury in algae. It is emphasised that the levels of the metal in water are very low, i.e. levels which would not normally be considered toxic to biota, yet the concentrations in biota from the field studies are sufficiently high to warrant concern for consumers.

In order to test the hypothesis that increased concentration of mercury in biota is a result of pH-dependent changes in the bioavailability of the metal, simple laboratory model food chains have been designed to determine the effect of pH on direct uptake of mercury into algae, herbivores and fish, and food chain transfer of mercury. The design and rationale will be presented, along with preliminary results.

The same pH-related bioconcentration in fish has recently been shown for cadmium and lead. The same experimental approach will be used to determine the bioconcentration of these two elements.

Number 14

A. Vajdic
Ministry of the Environment

TRACE CONTAMINANTS IN WATER TREATMENT PLANT CHEMICALS

ABSTRACT

Trace contaminants, potentially harmful to the health of consumers, may be present in drinking water because of contamination of the raw water source, or because they are introduced during the water treatment process. This study was designed to determine the extent to which water treatment chemicals may be contaminated, the variation in quality of such chemicals, and the actions which may be necessary to establish effective procedures for the delivery, examination and use of water treatment chemicals.

Results show that chemicals used by water treatment plants are not significant sources of contaminants in drinking water. The effects that some of the detected variations in chemical quality could have upon the treatment process are discussed.

Abstract for MOE Technology

Transfer Conference November, 1983

Experimental and Environmental Modelling Studies of Hazardous Substances in Ontario

D. Mackay, S. Paterson, B. Cheung and W.Y. Shiu
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University of Toronto

It is widely accepted that assessment of the behaviour of toxic chemicals requires the use of mathematical models which may be applied to actual or evaluative environments. In this project a version of the Fugacity Model has been developed and is being applied to a number of selected chemicals, namely the chlorobenzenes, the chlorophenols, mirex, atrazine and trichloroethylene. The evaluative model is designed to be applicable to the Ontario environment. Attempts are being made to obtain emission rate data and environmental monitoring data which can be used to calibrate the model.

A major aspect is the quantification of concentration heterogeneities and the inclusion of such concentrations as distribution functions of the lognormal or Weibull type. The feasibility of presenting the data in computer - generated colour contour form is being investigated.

Finally, methods of including toxicity information are being examined and will be discussed.

Number 16

ABSTRACT

REVISED MONITORING SCHEME FOR PERSISTENT AND TOXIC ORGANICS IN GREAT LAKES SPORTS FISH

J.A.Coburn and H.Huneault, ZENON ENVIRONMENTAL INC.

Screening protocols for the extraction of a broad range of synthetic organic compounds have been evaluated on fortified and unfortified fish tissue samples. Recoveries of the trace organics have been determined at low parts per million and parts per billion concentrations. Sample extracts were processed using gel permeation chromatography (GPC) for elimination of lipids from the trace organic fraction prior to full scan gas chromatographic-mass spectrometric (GC/MS) analysis. Data will be presented on the sample preparation protocols, GPC fractionation and preliminary GC/MS analyses of Great Lakes fish samples.

Number 17

Ian R. Smith* and V.E.O. Valli*, 1983. The Development of a Freshwater Fish Test to Identify Aquatic Toxic Contaminants**. Ontario Ministry of the Environment Technology Transfer Conference No. 4, Conference Proceedings, Toronto, Ontario, Nov. 29-30, 1983.

ABSTRACT

Determining the potential long and short term health effects of many of the chemicals being discovered in Ontario's receiving waters requires that new test approaches be developed. The most obvious way to study aquatic contaminants is to utilize aquatic species, however it is obvious that the development of new approaches to assess health effects in aquatic species has not kept up with the rate at which new chemicals of interest are being discovered. Gross genetic damage is a feature of many chemicals reacting with DNA, and in this study two endpoints indicative of chromosome breakage, anaphase aberrations and micronuclei, were assessed for their sensitivity. Exposure of Brachydanio rerio (Zebrafish) embryos to Ethyl Methanesulphonate (EMS) for up to 24 hours resulted in an increase in anaphase aberration frequency, and in aberration severity, in as little as 6 hours when exposed to 100 mg/L or 24 hours when exposed to 1 mg/L. Micronuclei were induced in 24 hours with 100 mg/L EMS, however further analysis of this approach's sensitivity is pending. 1000 mg/L EMS is non-lethal to embryos over the 24 hour exposure period, however a reduction in developmental stage (growth) was seen in 100 mg/L at 12 hours. It is apparent that both anaphase aberrations and micronuclei are sub-lethal phenomenon. A time and dose-dependant increase in anaphase aberrations was present, and our experiments show that this approach is perhaps the most sensitive short-term genotoxic assay yet reported in fish. The impact of chemicals on somatic and germinal DNA is an important and growing area of study because these genotoxicants are linked to carcinogenesis, teratogenesis, mutagenesis and long-term changes in the gene pool in mammals; this is just beginning to be shown with non-mammalian eukaryotes. The induction of genetic damage at sub-lethal levels has tremendous implications for both individuals and populations and this test system may provide a means for detecting and assessing waterborne genotoxic chemicals utilizing a fish species, in addition providing a link between existing bacterial and mammalian test procedures.

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** Supported by the Ontario Ministry of the Environment as Provincial Lottery Project No. 64.

Number 18

J. Easton

Ryerson Polytechnical Institute

THE EVALUATION AND APPLICATION OF PULSED NUCLEAR MAGNETIC RESONANCE IN THE ANALYSIS OF ENVIROMENTAL SAMPLES

The possibility of applying the low resolution pulsed N M R technique to the analysis of enviromental samples is described. The transversal magnetization for solids decays much faster than that of liquids. Comparison of the magnitudes of the total magnetization measured at different times can be used to determine the solid/liquid ratio or the percentage of liquid in a sample. The theoretical basis will be described along with the assessment of some of the microprocessor programs presently available for the analysis for appropriate samples.

Number 19

"Aquatic Toxicity Studies of Multiple Organic Compounds: The Concentration Addition Model"

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Abstract

A discussion of the various models proposed by aquatic toxicologists for predicting the joint toxicity of mixtures of organic compounds from their individual toxicities is presented. The rationale for adopting the "concentration addition model" as the most relevant to acute toxicity in fish is demonstrated by mixture data generated by our research group on chlorinated benzenes and phenols.

Whether or not concentration addition can successfully predict chronic effects such as fish growth presently remains uncertain because of an inadequate data base for individual chlorinated benzenes and phenols.

Bioconcentration data on chlorinated benzene mixtures clearly demonstrates that this group of organics bioconcentrate in fish independently of each other, which is consistent with concentration additivity. However, independent bioconcentration is only successful as a predictive model when BCFs are compared on a lipid weight basis.

Number 20

ABSTRACT

REMOVAL OF HAZARDOUS CONTAMINANTS IN WATER POLLUTION CONTROL PLANT EFFLUENTS

R. J. Rush and L. J. Taylor
Canviro Consultants Ltd.

Until very recently, relatively little was known about the identities and quantities of hazardous contaminants (HC's) entering wastewater treatment plants and little information was available on the factors which would influence their treatability and ultimate fate. Currently in Canada, the data base for HC's occurrence and removal at WPCP's is very limited. Therefore, in August 1982 a study was initiated to provide an accurate estimate of the annual loading of hazardous contaminants entering and being discharged from an Ontario WPCP, in order to determine the present sewage treatment process efficiency and factors influencing HC's removal. Monitoring included selected HC's such as PCBs, pesticides, PAHs, metals and conventional pollution parameters.

The study, which is still in progress, was divided into two phases. In Phase I, sampling was performed at the WPCP on two separate occassions in order to optimize site sampling techniques and analytical methods. Phase 2 involved collecting and analyzing 24 hour composite samples during three separate periods:

1. Winter (December 1982 and January 1983)
2. Spring (April and May 1983)
3. Summer (June to August 1983)

The selected parameters were determined in the raw combined influent and final effluent. The in-plant return was also monitored on certain sampling days. The WPCP operation was observed closely during the sampling periods and any operational upsets were recorded for correlation with the analytical results.

Chemical analyses and evaluation of the data are on-going. A progress report summarizing the study methodology and results available to date will be presented.

Number 21

Towards an Electrochemically-Based Chemoreceptive Membrane for Trace Atmospheric Organics

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Natural chemoreception provides a model for development of selective organic sensing where the basic premise of operation implies that transduction of a selective binding event occurs via change of electrochemical conductance features across sensing membranes. This work describes the construction and theory of an ammonia gas sensor based on an artificial bilayer lipid membrane (BLM) which was modified for selectivity with the antibiotic nonactin. Detection limits are presently in the 10^{-6} M range and selectivity coefficients for ammonia over methylamine and other similar organic species are extremely high. Presently limitations of sensitivity and selectivity are determined by the chemistry of the BLM. This has been investigated with respect to transmembrane ion conduction energy barriers and the alteration of the inherent membrane dipolar potential for development of a more generalized mechanism for signal transduction through employment of selective receptors. Preliminary results of Langmuir-Blodgett thin-film deposition technology for the production of stable organized membranes suitable for routine laboratory sensing will also be described.

Number 22

METHODS OF SAMPLING AND ANALYSIS OF ASBESTOS AIR POLLUTION IN ONTARIO

D. Verma
McMaster University

Abstract

Asbestos, a known fibrogenic and carcinogenic material, has been identified in the past as the problem associated with occupational environments. It is estimated that almost half of all occupationally related cancers are caused by asbestos. Asbestos disease of clinical significance is probably undetectable at low levels of exposure. Some malignancies, particularly mesothelioma appear to be associated with surprisingly low levels of exposure. This accounts for the importance of asbestos pollution of outdoor air as well as of indoor air (eg. schools and offices) of Ontario.

This presentation will report on the ongoing research funded by the Ministry of the Environment's Air Resources Branch. The rationale for research issues will be discussed. Data on the examination of methods for sampling and analysis of low levels of asbestos including various electron microscopic techniques will be presented.

Number 23

DETERMINATION OF METALS AND METAL COMPOUNDS IN AIR AND RELATED SAMPLES

J. C. Van Loon, Institute for Environmental Studies
University of Toronto

Work has been concentrated into 2 main areas, a study of Hg compounds in air and water and the direct introduction of air filter samples into an inductively coupled plasma and multitrace element analysis by emission spectrometry.

A. Mercury Compounds in Air and water

A study was made of the gas chromatographic - atomic absorption determination of dimethylmercury and methylmercury chloride in air. Parameters studied include: type of column packing, the influence of the composition of column, transfer line and injection valve surfaces, need for atomic absorption background correction and the efficiency of collection of the compounds. A procedure suitable for analysing building and street air was developed for the determination of dimethylmercury and methylmercury chloride (1). A Tennax column was employed and the temperature program was 150°C to 180°C at a rate at 20°C per minute. Organo mercury results of typical building and urban street air samples will be given. The detection limits for dimethylmercury and methylmercury chloride are 2 and 5 ng respectively. Preliminary results using a microwave plasma in emission as a detector for the gas chromatograph indicate that detection limits may be as much as 10 to 100 time better. A method is being developed for the determination of Hg compounds in water. An extraction of the compounds from samples acidified with HBr into a mixture of benzene and toluene was employed. The

latter is carefully evaporated to small volume and an aliquot injected into the gas chromatograph.

B. Direct Analysis of Air Filters

A Perkin-Elmer HGA 2100 was used to produce a vapour of air filters samples. The vapour was carried into the plasma in the sample carrier gas flow. This avoids the need for wet chemical sample treatment and the inherent problems due to losses and contamination. The Procedure involves taking a sample of a glass fiber filter paper using a paper punch. This sample is placed on a graphite platform. The platform is inserted into and centered in the graphite furnace. The furnace is purged with Ar and the flow rate through the furnace is adjusted to the optimum value of 400 ml/min. The sample is volatilized into the furnace. For refractory elements the Ar carrier gas is doped with 0.2% freon (helps volatillize elements as F or Cl compounds). Results have been obtained for Cu, Pb and V. Typical values for Pb and Cu are 4(9) ug/in^2 and 4(3) ug/in^2 respectively (average of several filters). The bracked values were obtained by wet chemical methods. Values for V will be reported at the seminar.

METHODOLOGICAL ISSUES RELATED TO THE ASSESSMENT OF THE HEALTH EFFECTS OF AIR POLLUTION.

P. Corey, Ph.D., F. Silverman, Ph.D., S. Mintz, M.D., and H.R. Hosein, Ph.D.
The Gage Research Institute, Departments of Medicine, and Preventive Medicine and Biostatistics, University of Toronto, Toronto, Ontario.

Health impact of low levels of air pollution is difficult to establish. Questions exist as to the most appropriate assessment of exposure. Because individuals can live some distance from fixed outdoor monitoring sites, which have been used to assess exposure in most studies and can spend up to 90% of their time indoors, the need for better estimates of exposure has arisen. Also previous studies have largely used severe symptoms or signs as measures of health effects ignoring minor fluctuations in disease in, for example, patients with pre-existing lung disease. We designed a study to address some of these problems.

Thirty asthmatics and fourteen healthy non-asthmatics were each visited on up to twenty days both in the morning and afternoon. On each day pulmonary function was assessed in the morning [including forced vital capacity (FVC), forced expiratory volume in one second (FEV_1) and maximum mid-expiratory flow rate ($FEF_{25\%-75\%VC}$)]. A personal multi-pollutant sampler [for sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and suspended particulate matter (SPM)] was then carried by the individual for the rest of the day at which time it was shut off. Pulmonary function was measured again and a questionnaire was completed documenting symptoms, medications, daily activities and exposure to potential household irritants. An estimate could be made of pulmonary function on a given day and the change over the day.

Cross-sectional analysis is often employed to establish a relationship between exposure to hazardous substances and response. In our study this consists of correlating across individuals, air pollutant concentrations with measures of health. A serious drawback to such an analysis is the confounding influence of a cohort effect which can lead to paradoxical findings such as healthier individuals being found associated with higher levels of pollution. A longitudinal analysis attempts to circumvent this problem by measuring within individuals the relationship between exposure and response. Results of our study will be discussed in relation to these two analytic approaches.

Number 25

R. Hughes, R. March
Trent University

A Mass Spectrometric Study of Selected Air Pollutants

Among the growing list of environmental pollutants present in the atmosphere is a class of multiple fused-ring aromatics known as Polycyclic Aromatic Hydrocarbons (PAH). Only a small number of these PAHs and related heterocycles such as anthracene, pyrene and carbazole are produced in pure form for industrial purposes, however many are produced whenever organic material is heated above 700 ° C, such as in pyrolysis or incomplete combustion. Furthermore, if the starting materials contain heteroatoms such as nitrogen, oxygen and sulphur the the products will contain a variety of related heteroaromatic compounds.

In general, PAHs are found everywhere in the environment and concern over their presence stems from the carcinogenicity of some members of this group such as benzo[a]pyrene. More recently concern has grown due to a degree of excess carcinogenicity from both urban air and exhaust particulates from combustion engines, which could not be accounted for solely on the basis of their measured content of benzo[a]pyrene and other related PAH. It has now been shown that PAHs can combine with other priority pollutants such as nitrogen oxides(NO_x), sulphur oxides(SO_x), ozone(O_3) and peroxy acetylnitrate(PAN). Furthermore this process may be facilitated by the adsorption of PAHs onto the surface of small particulate organic matter(POM) in the respirable(1 micron) diameter range. Thus the problems in urban atmospheres can be compounded by the production, from inactive PAH, of substituted PAHs which are active in the Ames microsomic mutagenicity test.

It has been found that the reaction of benzo[a]pyrene with NO_2 at 300 ° C gives rise to a variety of products including the mono-, di- and trinitro-derivatives which are presumably mutagenic in nature, as well as quinone derivatives some of which may be active and some of which are not. Prolonged heating of benzo[a]pyrene(12 hr.) with a molar excess of NO_2 in the ratio 5:1 or greater appears to result in the production of a lactone-quinone of molecular weight 300 amu. whose activity is unknown.

The storage of positively-charged benzo[a]pyrene and chrysene ions in the presence of NO and NO_2 has shown them to be unreactive under the conditions employed.

DEVELOPMENT OF A METHOD FOR MEASURING HYDROGEN PEROXIDE USING A TUNABLE DIODE LASER ABSORPTION SPECTROMETER

H.I. Schiff and D.R. Hastie

Department of Chemistry, York University

Hydrogen peroxide is believed to be the most important oxidant in transferring SO_2 to H_2SO_4. It is also closely coupled to the highly reactive HO and HO_2 radicals which are central to all chemical processes in the atmosphere. Measurements of the gaseous concentration of this species are therefore important in furthering our understanding, not only of acid deposition in particular, but of atmospheric chemistry in general.

We are developing methods to apply our tunable diode laser absorption spectrometer to measure hydrogen peroxide. The spectrometer combines the high resolution of a tunable diode with the sensitivity provided by a long-path White cell. It should be highly specific to hydrogen peroxide without interferences from other gases.

Laboratory measurements with this system have shown detection limits of 1 to 2 ppbv. Although such detection limits would be adequate for polluted air improvements would be desirable for clean air measurements. We are currently investigating computer data aquisition and analysis techniques which we believe will lower the detection limits be a factor of three or more.

Field measurements also require development of suitable calibration and sampling techniques. Both these requirements present formidible problems in the case of hydrogen peroxide. We are currently examining several sources of gaseous hydrogen peroxide which might serve to provide known concentrations for calibration purposes. We are also investigating the problems associated with sampling this highly polar gas. The results of these investigations will be presented.

Number 27

The Dispersal of Airborne Particulates on a Short and Long Term Basis

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The environment receives many substances from anthropogenic and natural sources. In order to understand their extent and effect, many measurements of various types are necessary. Proton induced X-ray emission has been used to measure the element concentrations at the ng/m^3 level in air particulates collected by means of an air streak filter which provides temporal records on a short time scale of about an hour. Also concentrations have been measured at the ppm level in tree rings which provide a temporal record over many years.

Two species of pine trees at each of two locations, one near and downwind and the other relatively distant and upwind from Sudbury have been examined to determine the effect of the smelters in that city. No distinctive differences attributed to the installation of the high INCO stack in 1973 were observed. However, the cores of trees taken from near Sudbury showed increased concentrations for most of the elements, S, Cl, K, Ca, Mn, and Fe. When scans of the concentrations were measured with a beam of 25 μm, variations in the levels of several of the elements were observed during the growing season.

Streak filters were taken during a three week sampling period last winter at ground level some 50 m from a busy intersection in Kingston. Large variations in the levels of several elements were detected and these correlated highly with vehicular traffic. This was especially true for lead. Furthermore, Na, Cl and Ca levels were strongly correlated, suggesting a common origin which might be the sanding mixture since the residual fine road dust showed high levels of these elements. Daily averages for the concentrations observed inside and outside a school at the site were also measured.

Number 28

Assessment of impact of oxidant injury on development of early blight on potato: implications for disease control.

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Some cultivars of potato grown in Ontario are very sensitive to O_3 and can sustain a lot of foliar injury some years. Some of these same cultivars like Norland and Norchip are very sensitive to early blight Alternaria solani.

The symptoms produced by O_3 or early blight when they occur alone are fairly distinct. When the two agents occur together a different symptom is produced. The new symptom is the result of the fungus infecting the many small lesions produced by O_3.

Reducing O_3 injury on sensitive cultivars increases the control of early blight by fungicides. Initial experiments were conducted with the antioxidant EDU which is no longer available. In 1983 plots were set up at a Research Station and in growers fields to determine whether fungicides with antioxidant properties, in combination with a fungicide effective in controlling early blight, would give better disease control.

Ozone injury and disease incidence were minimal until about mid-August. After that time considerable injury from both agents occurred. Because of the relative lateness in the season only two plots were still available for assessment. The effect of the fungicide manzate, which has antioxidant properties, and the effective fungicide, DuTer, applied singly or in combination, on foliar injury and yield will be discussed.

Production of Ozone Insensitive Field Bean Varieties

T.E. Michaels, W.D. Beversdorf, B.D. McKersie

Abstract

Common bean (Phaseolus vulgaris L.) suffers foliar injury following episodes of O_3 in excess of 9 pphm. Reductions in white bean yield due to O_3 have been estimated at 32-36% in southwest Ontario. Experiments conducted by the Department of Crop Science, University of Guelph with funding from the Ontario Ministry of the Environment were designed to identify intraspecific genetic sources of O_3 insensitivity, characterize the inheritance of O_3 insensitivity, and initiate breeding populations from which O_3 insensitive white bean cultivars could be derived.

A diverse group of field bean lines was screened for insensitivity in controlled and field conditions. Three lines classified as highly insensitive were intercrossed with adapted white bean cultivars to form breeding populations for inheritance studies and cultivar selection. The inheritance studies suggested that O_3 insensitivity is controlled by multiple nuclear genes. Heritability estimates from controlled environment screening were high (H=0.66-0.88) while estimates from field data were lower (H=0.16-0.21). These levels of heritability indicate that selection for ozone insensitivity can be effectively integrated with selection in the field for other quality, architectural and yield characteristics as breeding populations approach homozygosity.

Recent screening for insensitivity has relied on the natural occurrence of high ozone levels in field plantings of adapted cultivars, breeding populations, and new plant introductions. In 1983, over 1000 plots at Elora, Woodstock, Ailsa Craig, Mitchell and Palmerston were rated for O_3 insensitivity. Variation

among plots for O_3 damage was apparent in cultivar trials at most locations. Single plants were selected from O_3 insensitive breeding populations at Woodstock for observation and increase in 1984 followed by yield trials in 1985. Promising new sources of insensitivity were identified in the International Bean Flowering and Adaptation Nursery. These additional sources will be recombined with adapted white bean lines to form new breeding populations for selection of future ozone insensitive cultivars.

Number 30

Sweet Corn and Green and Wax Bean Responses to Air Pollution in Southern Ontario

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Replicated field experiments were conducted in 1982 and 1983 at the University of Guelph-Ontario Ministry of Agriculture and Food Research Station at Cambridge, Ontario; at the Ontario Ministry of Agriculture and Food Horticultural Experiment Station at Simcoe; and at the Canada Department of Agriculture Research Station at Harrow. Randomized block split-plot experiments were conducted with three concentrations of benomyl as a chemical protectant spray or drench, applied to plants weekly. Appropriate benomyl concentrations were established in laboratory studies with sweet corn and from literature references for beans. There were six cultivars of sweet corn and of snap beans at each location. Tobacco ozone-indicator plants were placed in each plot. The 1982 harvest data indicated that while there were substantial differences among yields of cultivars at each location, the relative differences were generally similar at all locations. The few changes in cultivar yield patterns may have reflected differences in temperature, rainfall, and other environmental responses, as well as differences in sentivitity to air pollution. There were few statistically significant effects of benomyl sprays in these studies. The effect of 4000 ppm sprays was injurious in some cases, particularly in the sweet corn experiment at Simcoe. Yield increases with 1000 ppm benomyl sprays were noted in some corn cultivars at Cambridge, and generally in corn at Harrow and in beans at Cambridge. Additional measurements made at the sweet corn harvest indicated that the benomyl effects on husk weight was always similar to that on total yield while cob number was significantly increased by benomyl only at Cambridge and cob size increased only at Harrow. Harvests and data analysis for the 1983 field experiments are not yet complete, and will be reported later.

Number 31

Abstract for MOE Technology

Transfer Conference November, 1983

Evaluation of Contaminated Water and Soil Sites as Sources of Airborne Hazardous Materials

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University of Toronto

The status of an experimental program supported by the Air Resources Branch is described in which the aims are to develop methods of quantifying emissions (i.e. source strengths) of organic contaminants from water bodies and from soils. The approach has been to design and operate a small scale system in which water containing dissolved contaminant is subjected to air and water turbulence which can simulate any desired environmental condition, as may exist in a lake, pond, river or lagoon. A similar system has been devised for soils. Attempts are being made to develop relatively simple mathematical models which can be used to correlate the experimental data and predict emission rates in other systems from a knowledge of the water or soil properties and the contaminant's physical chemical properties.

Number 32

Authors: R.B. Caton, S.G. Guerin and C.S. Davis
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Downsview, Ontario
and
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Ontario Ministry of the Environment,
Air Resources Branch,
Toronto, Ontario

ABSTRACT

The alternative sampling methods evaluated involved the modification of the standard Hi-Volume sampler by the addition of solid sorbent cartridges (polyurethane foam (PUF), XAD-2 and florisil) and an ozone denuder. Airborne particulate matter collected for a site in Hamilton were analysed by HPLC for fluoranthene, benzo(a)anthracene, pyrene, benzo(a)pyrene, 3 methylcholanthrene, benzo(g,h,i)perylene and dibenzo(a,i)pyrene. Laboratory and field studies were carried out to evaluate the performance of these samplers and to determine the effects of ozone and temperature on the collection of PAHs. The PUF and XAD-2 proved to be the better sorbents in view of their greater efficiency for capturing the more volatile PAHs lost from the filter (fluoranthene and pyrene especially) and their lower resistance to flow. A potential solution to the problem of the reaction of PAHs collected on filters with ozone has been obtained by the addition of an ozone denuder to the Hi-Volume sampler with a backup solid sorbent cartridge. The addition of ozone denuder and a versatile cartridge - capable of accommodating variable amounts of solid sorbents, have been demonstrated to be feasible, practical and effective modifications to existing Hi-Volume samplers for the sampling of airborne PAHs. Such samplers would not only allow quantitation of PAHs in airborne particulates - free from artifacts due to variation with ozone, but also allow sufficient sample to be collected for mutagenicity and other tests.

Number 33

Laser Induced Emission Spectroscopy of Polycyclic Aromatic Hydrocarbons (PAH) in Low Temperature Matrices

by F.J. Morgan, S.V. Filseth, and C.M. Sadowski
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Accurate identification and determination of trace amounts of PAH compounds in environmental samples is a prerequisite to any sensible attempt to set clean air standards. Emission and absorption spectroscopy have provided satisfactory data for inorganic compounds, but have been hampered from doing so for PAH compounds by the broad spectral features of such compounds at room temperature. Moreover, characteristic spectral lines are needed for a useful identification and determination technique. Shopolskii spectroscopy, in which samples are dissolved in normal alkanes (e.g. heptane) and then cooled to low temperatures (15°K), can give the necessary narrow line-like features. Then, radiation of any wavelength shorter than the threshold for a transition from the ground state of the PAH compound to its first singlet electronic level can be used to produce emission characteristic of that compound. However, some excitation wavelengths will be more effective than others, and these wavelengths will vary from compound to compound. Hence a tunable, high intensity, narrow band excitation source is desirable. We use a pulsed, tunable dye laser in conjunction with a closed cycle helium refrigerator to investigate Shpolskii spectra of individual PAH compounds. Then, these spectra can be used to identify and determine particular PAH compounds present in environmental samples. We shall describe our technique, discuss our results for some PAH compounds, and also describe our initial attempts to analyse environmental samples obtained in the Hamilton, Ontario area by Concord Scientific Corportation of Toronto.

Number 34

Sampling and Analysis of PAH Derivatives in Urban Air Particulates

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The chemical composition of urban air particulate matter is very complex, consisting of hundreds of organic and inorganic components. Over the last decade, many efforts have been directed to the determination of the levels of known carcinogenic compounds, particularly polycyclic aromatic hydrocarbons (PAHs) such as benzo-(a)-pyrene, in the organic solvent extractable fraction. In recent years it has become clear from work with microbial mutagenesis assays and chemical fractionation techniques that there are many hazardous substances present that are still largely uncharacterized. Studies have shown that much of the mutagenic activity in air particulate extracts is associated with compound classes other than the PAHs and that much of the activity is of the "direct-acting" type (1). Several studies have shown that nitrated and oxygenated polycyclic aromatic hydrocarbons (nitro-PAHs and oxy-PAHs) are probably the principle direct-acting mutagens in automobile exhaust and urban air particulate samples (2,3). The environmental significance of these mutagens is not yet fully established, however, due in part to the lack of analytical methods for their determination and in part to the fact that many of these compounds may be formed as artifacts during the sampling step. Recent studies have shown that some PAHs can react readily with filter media, nitrogen oxides, sulfur oxides, ozone, and gas-phase photochemical smog to form a variety of derivatives (4). We have developed a routine analytical method that is sensitive and selective for the determination of nitro-PAHs in environmental samples, such as diesel exhaust and urban air particulates (5). The key step in the procedure is a clean-up scheme that isolates the nitro-PAHs from the other components in the sample. The present project is concerned with adapting these analytical methods to the determination of both nitro- and oxy-PAHs. We are also attempting to determine the extent to which these PAH derivatives are artifacts of the sampling procedure and to investigate new methods of sampling.

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APPLICATION OF BENZAMIDE DIRECTED METALATION STRATEGY IN SHORT AND REGIOSPECIFIC ROUTES TO PERI-METHYL SUBSTITUTED PAH'S

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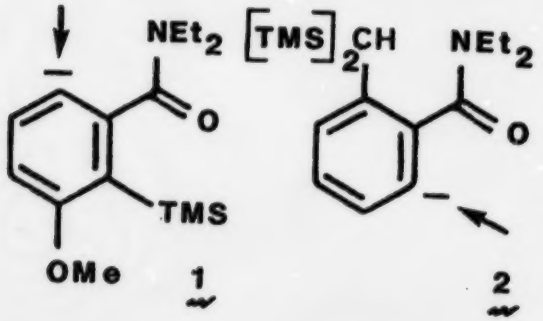
Number 35

As part of recent work on the strategy of benzamide directed ortho metalation (J.O.C. 1983, 48, 1568) we have shown that the $SiMe_3$ moiety is an effective protecting group for both aromatic sites and acidic methyl groups. Thus metalation (s-BuLi) of substrates **1** and **2** occurs exclusively at the sites indicated providing after quenching with a variety of electrophiles and subsequent desilylation (CSF/DMF-H_2O) diversely functionalized aromatics of the type **3** and **4** respectively. With substrates of type **1** Br^+-ion induced desilylation affords bromo aromatics **5** difficult to prepare by classical means, furthermore F^--ion induced carbodesilylation of **2** provides access to methyl substituted anthraquinones **6**.

These concepts have been used to develop short and efficient routes to peri-methyl substituted benz[a]anthraquinones of the type **7** and **8**, precursors to the corresponding PAH's of environmental interest. The above methodology will be detailed and the application to the synthesis of methyl substituted PAH's will be described.



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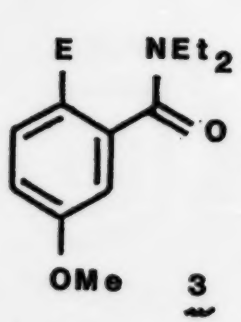

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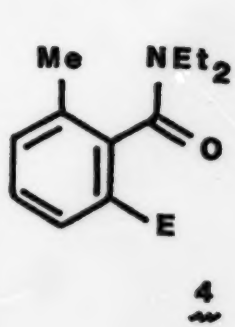

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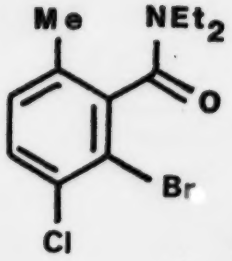
TMS = $SiMe_3$



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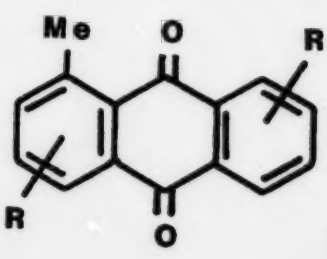

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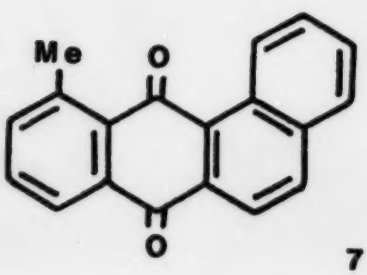

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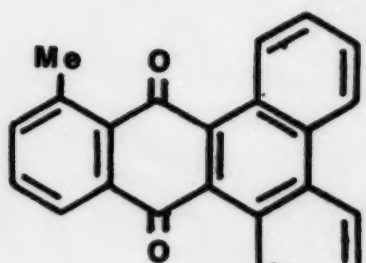

8

Number 36

E. Lee-Ruff, Department of Chemistry
York University

Project Title: Syntheses of Polynuclear Aromatic Hydrocarbons of Interest in Environmental Pollution

Abstract: We have synthesized a number of cyclopenteno-annelated and heterocyclic polynuclear aromatic hydrocarbons (PAH) to be used as standards for characterization of PAH's of unknown structures in air samples. These are related to the ubiquitons environmental PAH's: beno(a)pyrene and cyclopenta(c,d)pyrene. The syntheses involve a route using cyclobutanones as intermediates developed in our laboratories.

Number 37

ABSTRACT

RETROSPECTIVE CORRELATION SPECTROSCOPY AND ITS APPLICATION TO ATMOSPHERIC MONITORING

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Centre for Research in Experimental Space Science, York University

A brief review is given of the concepts of analogue correlation spectroscopy. It was proposed and developed in a number of laboratories in the 1960's. A number of successful commercial field instruments have been developed for remote sensing the presence and concentration of molecular atmospheric contaminant species. These instruments often use a unique mechnical correlation mask for each species, and thereby sense one species at a time.

We have made a study of the potential of retrospective digital correlation spectroscopy to the concurrent sensing of a number of atmospheric contaminants, for each of which a unique digital numerical correlation mask is convolved with the digital observational spectrum.

The results of the "proof of concept" study are presented, and the current research programme which has numerical and observational components is described.

Number 38

Monitoring Genotoxicity in the Environment Using Sister Chromatid Exchanges in Mice. M.L. Petras, Department of Biology, University of Windsor, Windsor, Ontario.

Preliminary evidence in a study by B.N. Nayak suggested that sister chromatid exchanges (SCE) in both wild and inbred mice might provide us with a sensitive system for monitoring changes in environmental levels of genotoxic agents. This report describes attempts to increase the efficiency of the SCE test and some early results in testing the sensitivity of the system.

The SCE test involves differential staining of newly formed chromatids through the incorporation of 5-bromo-2'-deoxyuridine (BudR). BudR was introduced into mice by four routes and in several concentrations. Of these 80 mg/g body weight, serially injected intraperitoneally gave the most consistent results in both C3H (5.40±0.14) and wild mice maintained in the laboratory (5.56±0.12); BudR even in very high doses in drinking water resulted in poor differential staining; plain BudR tablets gave consistently high SCE values (9.07±0.58); and parafin coated tablets gave values which were low and consistent in C3H (4.18±0.10) but which fluctuated considerably in wild mice because in some cases very little BudR was absorbed. For subsequent work, serial injections were used although coated tablets may be more suitable if the quality of the coating process is improved.

For a monitoring system to be useable, a large number of samples must be examined which in this case means that it must be feasible to prepare a large number of slides efficiently. This was accomplished by reducing the handling of slides. After the cells were fixed on a slide, the slides were placed in a staining tray. Then the entire tray was immersed in Hoechst 33258 for 15 minutes, exposed to florescent lights while covered with Sorensen's pH 8.0 buffer and stained with Fisher's Giemsa. The slides were not handled individually until they were examined under a microscope. Besides permitting the staining of a large number of slides this technique also gave excellent differential patterns.

During the development of the above procedure the effects of two mutagens, mitomycin C (MMC) and methyl methanesulfonate (MMS) injected intraperitoneally into the mice, were examined. The MMC increased SCE levels up to threefold at 2 ug/g body weight and the MMS fourfold at 10 ug/g body weight. For a more natural introduction of mutagens, MMS was placed in the drinking water for 14 days. SCE values doubled with a total intake as low as 23 ug/g body weight of MMS and tripled with 90 ug/g body weight.

Thirty-two wild mice were also examined. These were collected from corn cribs in southwestern Ontario either before or shortly after the area was sprayed with pesticides. The two sets of samples differed significantly in SCE counts, 5.99±0.32 for the "prespraying" sample and 9.22±0.63 for the "postepraying" group. The latter also differed significantly from the baseline SCE values observed in laboratory mice (5.40±0.14).

Results obtained thus far continue to support the potential of the SCE technique for mutagen monitoring.

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Number 39

DEVELOPMENT OF A STRATEGY FOR PREDICTING THE IMPACT OF ODOROUS POLLUTANTS FROM FAST FOOD RESTAURANTS ON THE SURROUNDING COMMUNITY

by

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It is still not possible to accurately assess whether citizens who complain about odors from fast food restaurants in their neighborhoods are truly offended by the emissions or are protesting against the litter and noise often created by teenage patrons. Unfortunately, fast food operations do not normally affect the surrounding community enough to generate sufficient complaints for statistical analyses.

Consequently, public attitude surveys have been carried out to determine the general reactions of individuals, selected at random in the neighborhood of a fast food outlet, to 25 commonly encountered odors. The results show that, in general, people like the odors of baking bread, barbeques and roses, but are disturbed by garbage, sewage treatment plants and fast food restaurants.

On the basis of the survey results and documented real life complaints, field samples are being collected and subjected to odor panel evaluations in the laboratory. Correlation in terms of a recently developed Odor Impact Model, providing measures of detection, discrimination-recognition and complaint potential thresholds as well as degrees of complaints, will facilitate the interpretation of laboratory generated data in terms of the number and frequency of complaints from the public reacting to a neighborhood odor source.

The Odor Impact Model is being applied to three odor sources. A domestic garbage landfill site and a sewage treatment plant provide facilities for convenient air sampling as well as good complaint documentation. The fast food outlets are handicapped by inadequate complaint data. When it has been validated the model can be used by industry and environmental regulatory agencies to characterize existing and proposed sources of odors with respect to their potentials for causing adverse community reactions.

Number 40

CHEMICAL SPECIATION OF AIRBORNE PARTICULATES

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Although neutron activation analysis provides high sensitivity and a low analytical blank, it does not allow determination of the chemical state of the elements detected. A method has been proposed whereby organic vapours are used to form volatile complexes of inorganic constituents of airborne particulates. These complexes could then be volatilised, removed from the sample and collected for neutron activation analysis. If the complex formation and volatilisation occur at different temperatures for different compounds of the same element, chemical speciation of that element should be possible.

The reactions of acetylacetone and its fluorinated derivatives with compounds of cadmium, iron and chromium are being studied to assess their possible utility for speciation. It has been found that although cadmium and its compounds react with the ligands tested, these reactions are too slow to be useful in analysis. The reactions of iron and chromium, however, are more rapid. The experimental methods adopted for this work will be described, results obtained to date will be discussed, and the course of future research on this topic will be outlined.

In order to prepare for future field studies in speciation, research in neutron activation analysis is also being carried out. A new method for the analysis of gamma-ray spectra has been developed and compared with other methods previously reported in the literature. The method developed in this laboratory proved to be as accurate as most other methods and more reliable in peak detec-

tion and in the treatment of multiplet peaks than several previously proposed techniques.

A new approach to optimisation of analytical procedures for activation analysis is under study. This new method, simplex optimisation by advance prediction (S.O.A.P.), involves calculation of spectra expected under given conditions and application of this information to simplex optimisation. The optimisation of single-element neutron activation analysis can now be achieved and multielement activation analysis is now being implemented . The progress made in these areas and the work yet to be done will be briefly described.

Number 41

Vapour Phase Photolysis of Chlorinated Aromatic Hydrocarbons

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Abstract

Although there have been almost no published accounts of the vapour phase photochemistry of chlorinated aromatic hydrocarbons, the subject has potential environmental significance because typical aryl chloride pollutants are somewhat volatile. They therefore are potentially subject to solar degradation in the atmosphere. Our research is directed to studying the modes of photodecomposition of typical aromatic pollutants (chlorinated benzenes and biphenyls) under inert (N_2) and reactive (O_2) atmospheres.

In this presentation, the literature on aryl halide photochemistry is reviewed; since most of the previous studies have used solution phase conditions, we have attempted to indicate the extent to which any of the observations may be relevant to gas phase photochemistry. Finally, we present a brief account of the experimental procedures we are using, together with some preliminary results on product identification in the chlorobenzene series.

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